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ALKOXIDE-DIRECTED HYDRIDE ADDITION TO α,β-UNSATURATED SULTONES

Kamal M. Dawood,[a,b] Andrea Bramborg,[a] Ahmed F. Darweesh,[a,b] Katrin Spinde,[a] Victor Rogachev,[a,c] Anne Jäger,[a] and Peter Metz*,[a]

[a]Department of Chemistry, Organic Chemistry I, Technische Universität Dresden, Bergstraße 66, 01069 Dresden, Germany
[b]Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt
[c]Tomsk Polytechnic University, Department of Organic Chemistry, Leninstr. 30, 634050 Tomsk, Russia
Fax: +49(351)46333162
E-mail: peter.metz@chemie.tu-dresden.de

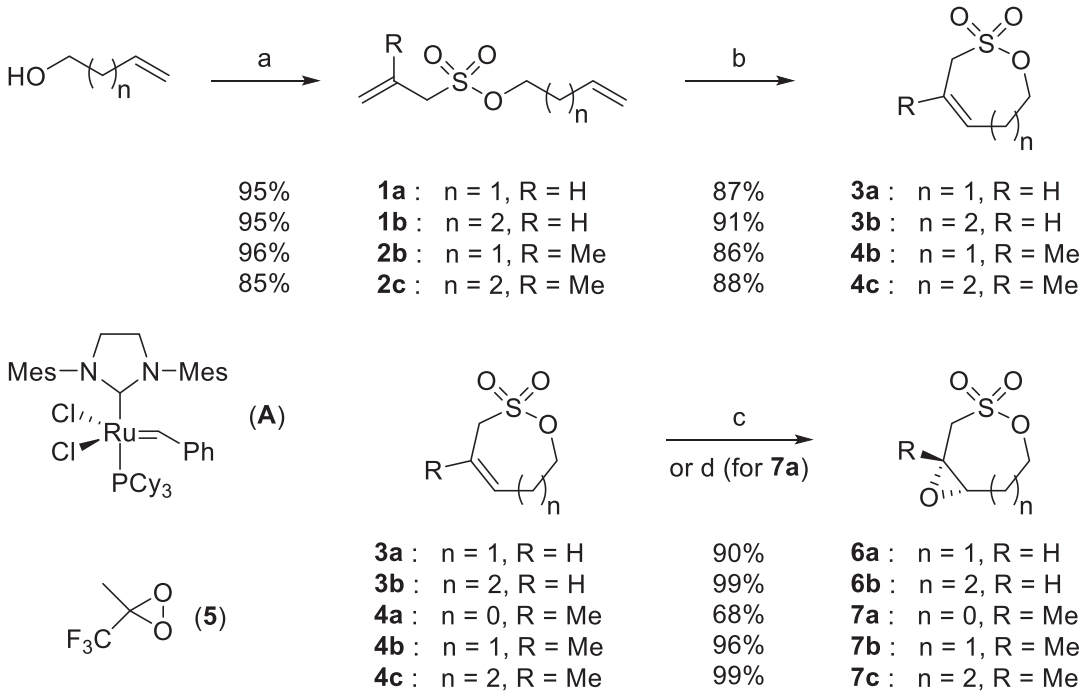
Abstract – Seven- and eight-membered β,γ-unsaturated sultones were readily prepared by ring closing metathesis. Epoxidation of these sultones and of an analogous six-membered sultone furnished the corresponding β,γ-epoxy sultones efficiently. Treatment of these epoxides with a suitable base gave α,β-unsaturated γ-hydroxy sultones in high yields. Reduction of both the α,β-unsaturated sultones and the epoxy sultones by Red-Al is likely to proceed in a hydroxyl-directed fashion via a mixed aluminate as the reactive intermediate.

INTRODUCTION

Sultones have drawn considerable attention due to their synthetic versatility and have been used as key building blocks in the total synthesis of natural products.[1,2] Applications of sultones in medicinal chemistry have been reported as well.[1,3] Several years ago, we published an investigation on the hydroxyl-directed reduction of bicyclic α,β-unsaturated δ-sultones with the sodium aluminum Red-Al.[4] This study was based on two earlier observations of domino elimination/alkoxide-directed reductions involving the intermediacy of α,β,γ,δ-unsaturated δ-sultones as extended conjugate acceptors.[5] Here we describe our recent results on hydride additions to various monocyclic α,β-unsaturated γ-hydroxy sultones with different ring sizes by Red-Al.

RESULTS AND DISCUSSION

As depicted in Scheme 1, we first prepared the β,γ-unsaturated sultones **3** and **4** by esterification of an appropriate hydroxy alkene with either allylsulfonyl chloride or 2-methylallylsulfonyl chloride[6a,b] to give the sulfonates **1** and **2**, respectively, followed by ring closing metathesis.[7] Next to the known sultones **3a** and **3b**,[7] the methyl substituted homologs **4b** and **4c** were isolated with good efficacy. Additionally, the δ-sultone **4a** was synthesized by a reported method through cycloaddition of sulfur trioxide to isoprene.[8] For a rapid high-yielding epoxidation of sultones **3** and **4**, methyl(trifluoromethyl)dioxirane (**5**)[9] was usually the reagent of choice, since the reaction with metachloroperbenzoic acid and also with dimethyldioxirane[10] was very slow. However, for the six-membered substrate **4a**, MCPBA proved to be superior.



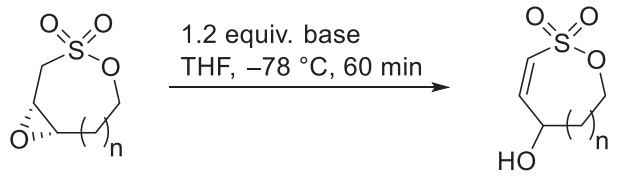
Synthesis of epoxysultones **6,7**. *Reagents and conditions*: (a) allylsulfonyl chloride (for **1a,b**) or 2-methylallylsulfonyl chloride (for **2b,c**), Et_3N, cat. DMAP, CH_2Cl_2, 0 °C, 1-2 h; (b) 2 mol% Grubbs II catalyst **A**, benzene, reflux, 1.5-2 h; (c) methyl(trifluoromethyl)dioxirane (**5**), $NaHCO_3$, MeCN, 0 °C, 1-2 h; (d) MCPBA, CH_2Cl_2, 0 °C to rt, 66 h.

Scheme 1

We then turned our attention to the generation of the desired α,β-unsaturated γ-hydroxy sultones by treatment of the epoxides **6** and **7** with different bases (Tables 1 and 2). As listed in Table 1, lithium diisopropylamide and lithium hexamethyldisilazide could be used for sultones **6a,b** to effect a rather clean epoxide opening triggered by deprotonation α to the sulfur atom in a short time at low

temperature. With both substrates LDA gave a slightly higher yield of elimination products **8a,b**. Methyllithium and butyllithium were less useful for this transformation.

Table 1. Synthesis of α,β-unsaturated γ-hydroxysultones **8a,b**

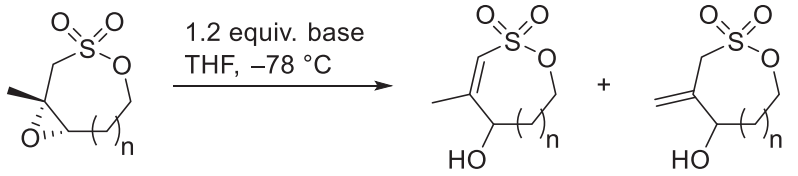


6a : n = 1
6b : n = 2

8a : n = 1
8b : n = 2

Epoxide **6**	Base	Alcohol **8**	Yield (%)
6a	LDA	**8a**	76
6a	LiHMDS	**8a**	58
6b	LDA	**8b**	74
6b	LiHMDS	**8b**	70

Table 2. Synthesis of α,β-unsaturated γ-hydroxysultones **9b,c**



7a : n = 0
7b : n = 1
7c : n = 2

9a : n = 0
9b : n = 1
9c : n = 2

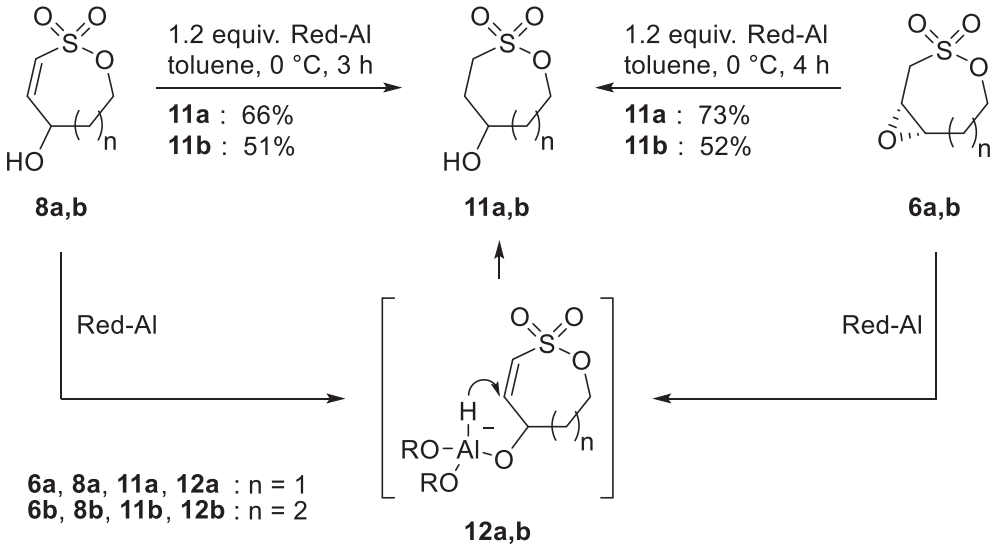
10a : n = 0
10b : n = 1
10c : n = 2

Epoxide **7**	Base	Time (h)	Yield (%)	
			9	**10**
7a	LiHMDS	3	96 (**9a**)	-
7b	LDA	23	10 (**9b**)	52 (**10b**)
7b	LiHMDS	3	95 (**9b**)	-
7c	LDA	9	16 (**9c**)	17 (**10c**)
7c	LiHMDS	3	96 (**9c**)	-

For the methyl substituted homologs **7b,c** (Table 2) lithium hexamethyldisilazide was clearly the preferred base that led virtually quantitatively to the desired products **9b,c** within a few hours. In contrast, LDA obviously also deprotonated the methyl group to give rise to the exocyclic olefins **10b,c**

in addition to **9b,c**. For conversion of the δ-sultone **7a** only LiHMDS was applied to produce **9a** as the sole isomer in excellent yield.

With the α,β-unsaturated γ-hydroxy sultones **8a,b** the Red-Al reduction was studied first (Scheme 2). Both the seven- and eight-membered substrate were converted to their saturated derivatives **11a,b** after a short reaction time at 0 °C. Presumably, the mixed aluminates **12a,b** formed by deprotonation of the alcohols **8a,b** with Red-Al are involved as reactive intermediates.[4,5] The saturated alcohols **11a,b** were again isolated as single regioisomers in comparable yields when epoxides **6a,b** were treated with Red-Al under the same conditions. These results can be readily rationalized by a domino elimination/alkoxide-directed hydride addition via the mixed aluminates **12a,b**, this time produced by deprotonation of sultones **6a,b** α to the sulfonyl group with Red-Al.

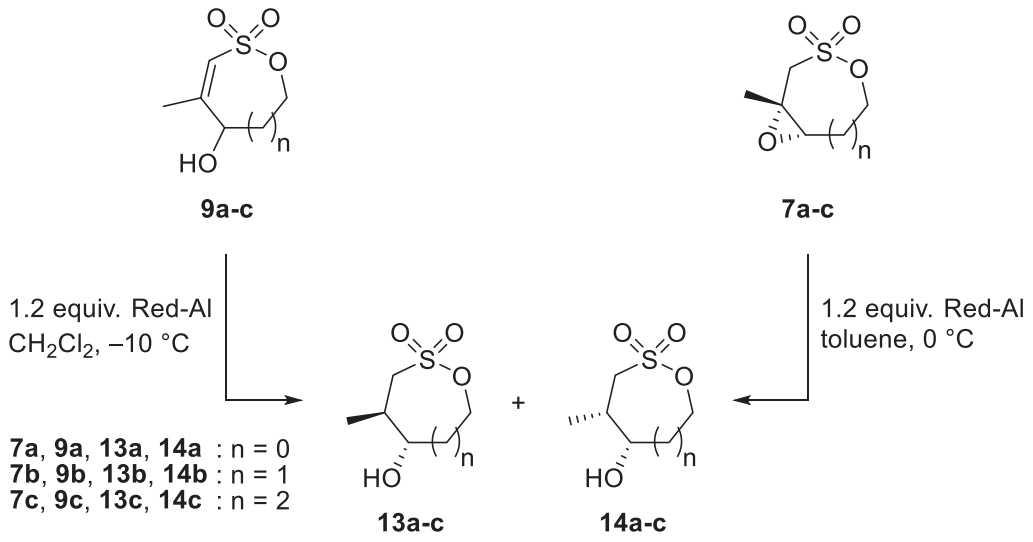


Scheme 2

In order to investigate the diastereoselectivity of this hydride addition, the methyl substituted α,β-unsaturated γ-hydroxy sultones **9a-c** were subjected to Red-Al (Table 3). For these substrates, dichloromethane turned out to be a more suitable solvent that allowed the reaction to take place rapidly at −10 °C already. Reduction of the δ-sultone **9a** proceeded with complete diastereoselectivity to deliver only the *trans* disubstituted sultone **13a**, albeit in rather low yield. The relative configuration of this compound was unambiguously established by X-ray diffraction analysis (Figure 1).[11,12] This stereochemical outcome lends support to the intermediacy of a mixed aluminate that undergoes an intramolecular hydride addition *syn* to the alkoxide directing group. Reaction of the seven-membered substrate **9b** with Red-Al was still highly *syn* selective to give the *trans* product **13b** as the major isomer as inferred from NOESY spectra of the two diastereomers. Interestingly, the substrate-induced

diastereoselectivity switched to an *anti* selective mode for the Red-Al reduction of the eight-membered sultone **9c**. The relative configuration of the resultant major *cis* isomer **14c** was again unequivocally determined by X-ray diffraction analysis (Figure 2).[11,12] A similar dependence of diastereoselectivity on the ring size has been noted for the hydroxyl-directed epoxidation[13] and Simmons-Smith methylenation[14] of cyclic allylic alcohols, where *anti* selectivity predominated for medium-sized rings. In a second series of experiments, the epoxy sultones **7a-c** were treated with Red-Al. As for the substrates **6a,b**, performing the reactions in toluene at 0 °C led to rapid conversion. To our delight, the *trans* disubstituted sultone **13a** was again formed exclusively from the δ-sultone **7a**, but now with a good yield of 62%. The seven-membered substrate **7b** reacted with a *syn* selectivity very similar to the corresponding transformation of the hydroxy sultone **9b**. Thus, these experiments also underpin a hydroxyl-directed pathway via a mixed aluminate of the type **12**. Only in the case of the medium ring sized epoxy sultone **7c**, the stereochemical result is significantly different from the outcome noted for the reaction of hydroxy sultone **9c**.

Table 3. Diastereoselective synthesis of γ-hydroxysultones **13** and **14**



Entry	Substrate	Time (h)	**13** : **14**	Yield **13** + **14** (%)
1	**9a**	1	only **13a**	18
2	**9b**	3	82 : 18	64
3	**9c**	3	12 : 88	70
4	**7a**	1	only **13a**	62
5	**7b**	1	87 : 13	43
6	**7c**	1	48 : 52	80

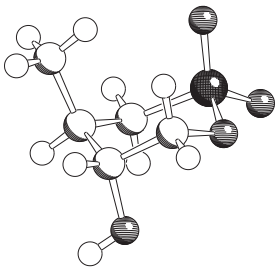


Figure 1. Crystal structure of sultone **13a**[11,12]

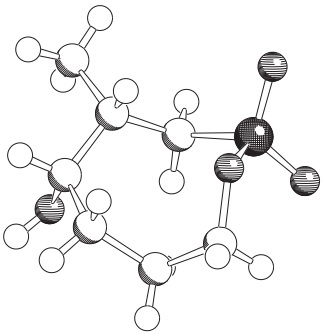


Figure 2. Crystal structure of sultone **14c**[11,12]

In summary, a range of novel functionalized monocyclic sultones was efficiently prepared by ring closing metathesis of unsaturated vinylsulfonates, epoxidation, and basic epoxide opening. Reduction of the resultant α,β-unsaturated γ-hydroxy sultones **8** and **9** as well as the epoxy sultones **6** and **7** by Red-Al is likely to proceed in a hydroxyl-directed fashion via a mixed aluminate as the reactive intermediate. Explanation of the exceptional stereorandom behaviour of the eight-membered epoxy sultone **7c** must await further studies.

EXPERIMENTAL

THF, dichloromethane, and toluene were dried and purified by passage through a MB-SPS-800 device using molecular sieves. Et_3N was freshly destilled over CaH_2. All other commercially available reagents were used as received. Reactions were performed under argon atmosphere. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} 0.2 mm precoated plates. Flash column chromatography was carried out using silica gel (Merck, particle size 40–63 μm). Melting points were measured on a Wagner & Munz PolyTherm A and are uncorrected. Infrared spectra were recorded on a THERMONICOLET Avatar 360 instrument using ATR. NMR spectra were recorded on a Bruker DRX 500 P (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometer or else on an Avance III 600 (^{1}H 600 MHz, ^{13}C 150 MHz) or an AC-300-P (^{1}H 300 MHz, ^{13}C 75 MHz). The multiplicities of ^{13}C NMR

signals were determined using DEPT spectra. Mass spectra were recorded with an Agilent 5973N detector coupled with an Agilent 6890N GC (GC-MS, 70 eV) and a Bruker Esquire LC (direct injection as a methanolic NH_4OAc solution, ESI). HRMS spectra were recorded on a Finnigan MAT 95 (EI, 70 eV). Elemental analysis was performed on a Hekatech EA 3000. X-ray analyses were carried out with a Bruker Kappa CCD diffractometer.

Synthesis of sulfonates 2b,c (general procedure)

The unsaturated alcohol (1.00 mmol) was dissolved in CH_2Cl_2 (10 mL), and a small amount of *N,N*-dimethylaminopyridine was added. The solution was cooled to 0 °C, and triethylamine (1.20 mmol) was added. Then, 2-methylallylsulfonyl chloride (0.186 g, 1.20 mmol) was slowly added with cooling and stirring. The resultant solution was stirred at 0 °C until complete conversion of the alcohol substrate (1–2 h). In order to remove triethylammonium hydrochloride, the mixture was filtered through a plug of silica gel, which was eluted with Et_2O. After removal of the volatiles under reduced pressure, the crude product was purified by flash chromatography on silica gel to give the sulfonates **2b** and **2c**.

Sulfonate **2b**. R_f 0.63 (pentane/Et_2O 2:1); colorless oil; IR 3083, 2982, 2924, 1644, 1431, 1351, 1255, 1170, 953, 902, 832, 765, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.99 (s, 3 H), 2.47–2.56 (m, 2 H), 3.81 (s, 2 H), 4.30 (t, J = 6.7 Hz, 2 H), 5.13–5.25 (m, 4 H), 5.73–5.87 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.3 (CH_3), 33.6 (CH_2), 58.4 (CH_2), 69.3 (CH_2), 118.4 (CH_2), 120.7 (CH_2), 132.4 (CH), 133.1 (C); GC-MS *m/z* 81 (6), 56 (6), 55 (100), 54 (21), 53 (7). Anal. Calcd for $C_8H_{14}O_3S$: C, 50.50; H, 7.42; S, 16.85. Found: C, 50.67; H, 7.66; S, 16.57.

Sulfonate **2c**. R_f 0.68 (pentane/Et_2O 2:1); colorless oil; IR 3082, 2980, 2925, 2848, 1642, 1448, 1351, 1292, 1253, 1171, 965, 912, 834, 735, 684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72–1.82 (m, 2 H), 1.90 (br s, 3 H), 2.06–2.15 (m, 2 H), 3.72 (br s, 2 H), 4.18 (t, J = 6.5 Hz, 2 H), 4.93–5.16 (m, 4 H), 5.64–5.79 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.3 (CH_3), 28.4 (CH_2), 29.4 (CH_2), 58.3 (CH_2), 69.8 (CH_2), 115.9 (CH_2), 120.6 (CH_2), 133.2 (C), 136.6 (CH); GC-MS *m/z* 84 (14), 81 (3), 71 (14), 69 (38), 68 (100), 67 (59), 55 (78), 53 (16), 41 (45), 39 (24). Anal. Calcd for $C_9H_{16}O_3S$: C, 52.91; H, 7.89; S, 15.70. Found: C, 53.02; H, 7.98; S, 15.19.

Ring closing metathesis (general procedure)

Sulfonate **2b,c** (1 mmol) was dissolved under argon in CH_2Cl_2 (100 mL), and the solution was heated to reflux. Grubbs II catalyst (2 mol%) was added to the refluxing solution in three portions, and the resulting mixture was stirred at reflux for 2 h. When the reaction was complete (TLC control), the mixture was cooled to room temperature, dimethyl sulfoxide (1 mmol) was added, and stirring was continued overnight. After removal of the volatiles under reduced pressure, the sultones **4b,c** were purified by flash chromatography on silica gel.

Sultone **4b**. R_f 0.47 (pentane/Et_2O 1:1); colorless crystals; mp 63–64 °C; IR 2968, 2922, 2851, 1445, 1407, 1341, 1285, 1169, 1008, 966, 933, 876, 849, 801, 788, 718, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83 (d, *J* = 1.1 Hz, 3 H), 2.42–2.51 (m, 2 H), 3.91 (s, 2 H), 4.39–4.45 (m, 2 H), 5.85 (br t, *J* = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.7 (CH_3), 28.3 (CH_2), 55.9 (CH_2), 74.0 (CH_2), 128.2 (CH), 129.5 (C); GC-MS *m/z* 162 (17) [M^+], 81 (100), 79 (26), 69 (12), 68 (59), 67 (62), 55 (7), 53 (32), 42 (9), 41 (29), 40 (12), 39 (27). Anal. Calcd for $C_6H_{10}O_3S$: C, 44.43; H, 6.21; S, 19.77. Found: C, 44.66; H, 6.34; S, 19.81.

Sultone **4c**. R_f 0.57 (pentane/Et_2O 1:1); colorless crystals; mp 39–40 °C; IR 3076, 2945, 2921, 2843, 1451, 1415, 1353, 1287, 1178, 1006, 969, 937, 873, 853, 806, 791, 708, 601 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–1.89 (m, 2 H), 1.89 (br s, 3 H), 2.19–2.29 (m, 2 H), 3.81 (s, 2 H), 4.29 (t, *J* = 5.9 Hz, 2 H), 5.58 (br t, *J* = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.8 (CH_2), 24.8 (CH_3), 26.9 (CH_2), 53.3 (CH_2), 71.2 (CH_2), 127.6 (C), 129.7 (CH); GC-MS *m/z* 176 (3) [M^+], 112 (18), 98 (7), 97 (100), 81 (9), 79 (16), 71 (11), 69 (6), 67 (27), 55 (23). Anal. Calcd for $C_7H_{12}O_3S$: C, 47.71; H, 6.86; S, 18.20. Found C, 47.97; H, 7.02; S, 17.86.

Epoxidation of sultone 4a with MCPBA

A solution of sultone **4a** (0.677 g, 4.57 mmol) in CH_2Cl_2 (15 mL) was cooled to 0 °C. Metachloroperbenzoic acid (75%, 1.367 g, 5.94 mmol) was added, and the resulting solution was stirred for 42 h while slowly warming to ambient temperature. After addition of more metachloroperbenzoic acid (0.550 g, 2.39 mmol), the solution was stirred for further 24 h. Then, saturated aqueous Na_2CO_3 solution was added, the layers were separated, and the organic layer was filtered. The organic layer was washed with saturated aqueous $Na_2S_2O_3$ and saturated aqueous Na_2CO_3 and dried over $MgSO_4$. The volatiles were removed under reduced pressure, and the crude product was purified by flash chromatography on silica gel (isohexane/EtOAc 2:1 to 1:1) to give epoxide **7a** (0.507 g, 68%) as a white solid.

Epoxide **7a**. R_f 0.36 (isohexane/EtOAc 1:1); mp 44.5–45.5 °C; IR 2984, 2964, 2940, 1692, 1485, 1442, 1353, 1303, 1253, 1208, 1185, 1156, 1075, 1051, 1006, 973, 932, 913, 863, 833, 804, 739, 696, 671 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (s, 3 H, CH_3), 3.03 (s, 1 H), 3.30 (d, *J* = 15 Hz, 1 H), 3.51 (d, *J* = 15 Hz, 1 H), 4.66 (d, *J* = 13.2 Hz, 1 H), 4.79 (d, *J* = 13.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.5 (CH_3), 51.2 (CH_2), 54.1 (CH), 56.8 (C), 68.5 (CH_2); MS (ESI) *m/z* 165 [$M+H^+$], 163 [$M–H^+$]; GC-MS *m/z* 121 (10), 107 (100), 43 (85). Anal. Calcd for $C_5H_8O_4S$: C, 36.58; H, 4.91; S, 19.53. Found: C, 36.47; H, 5.01; S, 19.29.

Epoxidation of sultone 4c with methyl(trifluoromethyl)dioxirane (typical procedure)

To a solution of the sultone **4c** (98.4 mg, 0.56 mmol) in MeCN (11 mL) cooled to 0 °C, was added an aqueous solution of 10^{-4} M Na_2EDTA (10 mL) and tetrabutylammonium hydrogensulfate (5 mg). Then a mixture of oxone (1.89 g, 3.08 mmol) and sodium carbonate (437 mg, 3.16 mmol) pulverized in a

mortar, was added in small portions to the solution over a period of 1 h, so that the pH always remained above 7. Meanwhile, 1,1,1-trifluoroacetone (12.5 mg, 0.11 mmol, 0.2 equiv.) was added portionwise during addition of the oxone/carbonate mixture. The resulting mixture was stirred vigorously at 0 °C for 2 h until complete conversion. The reaction mixture was treated with distilled water (100 mL) to dissolve the remaining solid, and the aqueous phase was extracted with CH_2Cl_2 (3x40 mL). The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ and saturated aqueous NaCl, and finally dried over $MgSO_4$. The solvent was removed under reduced pressure, and purification by flash chromatography on silica gel (pentane/Et_2O 1:2) gave epoxide **7c** (106 mg, 99%) as a colorless oil.

Epoxide **6a**. R_f 0.25 (pentane/Et_2O 1:2); white solid; mp 62–63 °C; IR 3001, 2845, 1467, 1440, 1387, 1377, 1346, 1267, 1256, 1165, 1099, 973, 922, 870, 809, 786, 706, 606 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00–2.09 (m, 1 H), 2.58–2.64 (m, 1 H), 3.22–3.27 (m, 1 H), 3.33–3.38 (m, 1 H), 3.43 (dd, *J* = 6.8, 15.3 Hz, 1 H), 3.99 (dd, *J* = 6.0, 15.3 Hz, 1 H), 4.37 (ddd, *J* = 2.1, 5.6, 12.5 Hz, 1 H), 4.59–4.65 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.0 (CH_2), 47.3 (CH), 53.0 (CH_2), 53.7 (CH), 68.6 (CH_2); GC-MS *m/z* 164 (0.1) [M^+], 121 (34), 93 (25), 70 (58), 65 (26), 57 (100), 55 (13), 45 (14), 44 (54), 43 (46), 42 (71), 41 (32), 39 (21). Anal. Calcd for $C_5H_8O_4S$: C, 36.58; H, 4.91; S, 19.53. Found: C, 36.39; H, 5.50; S, 19.12.

Epoxide **6b**. R_f 0.26 (pentane/Et_2O 1:2); mp 78–79 °C; IR 2992, 2949, 2848, 1468, 1435, 1387, 1347, 1260, 1173, 1009, 926, 877, 821, 776, 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25–1.40 (m, 1 H), 1.76–1.91 (m, 1 H), 1.99–2.15 (m, 1 H), 2.30–2.40 (m, 1 H), 2.98–3.10 (m, 2 H), 3.28–3.35 (m, 1 H), 3.85 (dd, *J* = 4.7, 14.6 Hz, 1 H), 4.30–4.39 (m, 1 H), 4.55 (ddd, *J* = 3.6, 10.6, 14.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.9 (CH_2), 24.0 (CH_2), 49.3 (CH), 50.1 (CH_2), 54.1 (CH), 71.5 (CH_2); GC-MS *m/z* 107 (1), 83 (1), 71 (100), 43 (52), 42 (6), 41 (30), 39 (10). Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66; S, 17.99. Found: C, 40.50; H, 5.50; S, 17.75.

Epoxide **7b**. R_f 0.21 (pentane/Et_2O 1:2); white solid, mp 49–50 °C; IR 2995, 2959, 2943, 1466, 1446, 1376, 1341, 1266, 1232, 1149, 1075, 969, 909, 873, 812, 762, 709 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (s, 3 H), 1.88–1.98 (m, 1 H), 2.49–2.58 (m, 1 H), 3.09 (t, *J* = 7.0 Hz, 1 H), 3.42 (d, *J* = 15.2 Hz, 1 H), 3.68 (dd, *J* = 0.5, 15.2 Hz, 1 H), 4.29 (ddd, *J* = 2.2, 4.9, 12.5 Hz, 1 H), 4.54–4.62 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.7 (CH_3), 31.8 (CH_2), 54.3 (C), 58.6 (CH_2), 60.2 (CH), 68.9 (CH_2); GC-MS *m/z* 121 (52), 93 (29), 84 (10), 81 (2), 69 (4), 65 (33), 58 (70), 57 (100), 55 (13), 54 (100), 53 (5), 45 (12). Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66; S, 17.99. Found: C, 40.70; H, 5.51; S, 17.19.

Epoxide **7c**. R_f 0.45 (pentane/Et_2O 1:2); colorless oil; IR 2998, 2963, 2939, 1473, 1454, 1387, 1344, 1261, 1239, 1157, 1079, 975, 913, 889, 815 cm^{-1};^1H NMR ($CDCl_3$) δ 1.54 (s, 3 H), 1.75–1.92 (m, 2 H), 1.96–2.12 (m, 1 H), 2.28–2.40 (m, 1 H), 2.80 (dd, *J* = 3.9, 11.0 Hz, 1 H), 3.18 (d, *J* = 14.8 Hz, 1 H),

3.59 (d, *J* = 14.8 Hz, 1 H), 4.32–4.53 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.2 (CH_3), 23.9 (2× CH_2), 55.6 (CH_2), 56.1 (C), 61.4 (CH), 71.5 (CH_2); GC-MS *m/z* 71 (100), 57 (5), 43 (50), 41 (27), 39 (17). Anal. Calcd for $C_7H_{12}O_4S$: C, 43.74; H, 6.29; S, 16.68. Found: C, 43.99; H, 6.46; S, 16.32.

Basic ring opening of epoxy sultones 6,7

Use of LDA (typical procedure)

To a solution of diisopropylamine (0.6 mmol) in dry THF (2 mL) cooled to −78 °C was added BuLi (2.5 M in hexane, 0.6 mmol) dropwise, and the resulting mixture was stirred at −78 °C for 30 min. To the resulting mixture was added a solution of epoxide **7c** (0.5 mmol) dissolved in THF (10 mL). After complete addition, the reaction mixture was slowly warmed to room temperature and stirring was continued for 9 h. The mixture was quenched with saturated aqueous NH_4Cl (10 mL), extracted with Et_2O (3x25 mL), and the combined extracts were dried over $MgSO_4$. After evaporating the solvent in vacuo, flash chromatography (pentane/EtOAc 1:2) furnished the unsaturated sultones **9c** and **10c** as colorless oils.

Use of LiHMDS (typical procedure)

To a solution of epoxide **7c** (0.5 mmol) in THF (10 mL) cooled to −78 °C was added LiHMDS (1.0 M in THF, 0.6 mmol) dropwise, and the resulting mixture was stirred at −78 °C for 3 h until complete conversion. The mixture was worked up and purified as above to furnish the unsaturated sultone **9c** as a colorless oil.

Sultone **8a**. R_f 0.29 (pentane/EtOAc 1:2); IR 3288, 3064, 2973, 2948, 1632, 1461, 1446, 1345, 1286, 1246, 1157, 1049, 1011, 938, 884, 811, 733, 677 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.12–2.18 (m, 1 H), 2.29–2.38 (m, 1 H), 2.69 (br s, 1 H), 4.47–4.52 (m, 1 H), 4.62 (ddd, *J* = 3.8, 10.5, 14.3 Hz, 1 H), 4.87–4.93 (m, 1 H), 6.49–6.56 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.2 (CH_2), 68.5 (CH), 68.9 (CH_2), 128.2 (CH), 147.1 (CH); GC-MS *m/z* 121 (36), 93 (26), 71 (6), 70 (59), 65 (29), 57 (100), 55 (13), 48 (5), 45 (14). Anal. Calcd for $C_5H_8O_4S$: C, 36.58; H, 4.91; S, 19.53. Found: C, 36.01; H, 4.54; S, 18.83.

Sultone **8b**. R_f 0.25 (pentane/EtOAc 1:2); mp 59–62 °C; IR 3403, 3053, 2927, 2863, 1629, 1446, 1333, 1217, 1156, 1047, 1026, 928, 876, 790, 725, 693, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.55–1.80 (m, 2 H), 1.90–2.18 (m, 2 H), 2.28 (br s, 1 H), 4.14–4.23 (m, 1 H), 4.53–4.59 (m, 1 H), 5.25–5.35 (m, 1 H), 6.08 (dd, *J* = 6.3, 11.8 Hz, 1 H), 6.34 (dd, *J* = 1.8, 11.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 23.7 (CH_2), 33.1 (CH_2), 67.7 (CH), 73.3 (CH_2), 126.8 (CH), 142.8 (CH); GC-MS *m/z* 149 (12), 137 (5), 119 (100), 113 (23), 109 (4), 97 (15), 86 (15), 83 (14), 71 (25), 70 (15), 68 (9), 65 (14), 57 (13), 56 (14), 55 (63), 43 (17), 42 (59), 41 (32), 39 (15). Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66; S, 17.99. Found: C, 40.12; H, 5.23; S, 17.38.

Sultone **9a**. R_f 0.55 (EtOAc); mp 48–49 °C; IR 3291, 3055, 2968, 2919, 2852, 2030, 1641, 1573, 1442, 1338, 1248, 1175, 1130, 1089, 1065, 1018, 947, 879, 847, 803, 750, 677, 612 cm^{-1}; ^{1}H NMR (300

MHz, $CDCl_3$) δ 1.90 (s, 3 H, CH_3), 2.55 (br d, *J* = 9.5 Hz, 1 H), 3.87–3.90 (m, 1 H), 4.45 (dd, *J* = 3.6, 12.6 Hz, 1 H), 4.69 (dd, *J* = 3.3, 12.5 Hz, 1 H), 6.18 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 64.4 (CH), 73.8 (CH_2), 121.7 (CH), 148.8 (C); MS (ESI) *m/z* 182 [$M+NH_4^+$], 187 [$M+Na^+$], 351 [$2M+Na^+$]; GC-MS *m/z* 146 (2) [$M–H_2O^+$], 134 (15), 116 (25), 88 (20), 69 (100). Anal. Calcd for $C_5H_8O_4S$: C, 36.58; H, 4.91; S, 19.53. Found: C, 36.44; H, 5.02; S, 19.28.

Sultone **9b**. R_f 0.32 (pentane/EtOAc, 1:2); mp 48–50 °C; IR 3412, 3058, 2932, 2876, 1632, 1449, 1332, 1212, 1157, 1047, 1029, 925, 876, 790, 728, 693, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.99 (s, 3 H), 2.10–2.17 (m, 2 H), 2.60 (br s, 1 H), 4.54 (t, *J* = 5.7 Hz, 2 H), 4.72 (br s, 1 H), 6.35 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.2 (CH_3), 33.9 (CH_2), 68.1 (CH_2), 70.5 (CH), 124.9 (CH), 156.8 (C); GC-MS *m/z* 178 (4) [M^+], 160 (4), 149 (27), 133 (33), 122 (10), 97 (17), 96 (13), 84 (54), 69 (100), 55 (17), 45 (12). Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66; S, 17.99. Found: C, 40.12; H, 5.09; S, 17.48.

Sultone **9c**. R_f 0.36 (pentane/EtOAc 1:2); colorless oil; IR 3421, 3056, 2921, 2867, 1625, 1451, 1341, 1227, 1152, 1047, 1023, 918, 866, 799, 729, 693, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.55–1.77 (m, 2 H), 1.88 (s, 3 H), 1.92–2.11 (m, 2 H), 2.35 (br s, 1 H), 4.13–4.23 (m, 1 H), 4.48–4.56 (m, 1 H), 5.44–5.52 (m, 1 H), 6.23 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 18.6 (CH_3), 23.8 (CH_2), 32.5 (CH_2), 68.6 (CH), 72.7 (CH_2), 123.0 (CH), 152.7 (C); GC-MS *m/z* 164 (6), 146 (8), 133 (100), 123 (8), 113 (31), 97 (29), 83 (11), 71 (14), 69 (48), 55 (11). Anal. Calcd for $C_7H_{12}O_4S$: C, 43.74; H, 6.29; S, 16.68. Found: C, 43.59; H, 6.03; S, 16.12.

Sultone **10b**. R_f 0.22 (pentane/EtOAc 1:2); IR 3518, 2926, 1420, 1338, 1157, 1061, 998, 955, 924, 901, 830, 732, 628 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.94–1.95 (m, 1 H), 2.07–2.19 (m, 1 H), 2.32–2.43 (m, 1 H), 3.93 (d, *J* = 14.3 Hz, 1 H), 4.36 (ddd, *J* = 3.5, 5.7, 12.8 Hz, 1 H), 4.44 (dd, *J* = 0.7, 14.3 Hz, 1 H), 4.61–4.70 (m, 2 H), 5.42 (s, 1 H), 5.53 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 37.4 (CH_2), 54.2 (CH_2), 66.4 (CH_2), 71.4 (CH), 121.5 (CH_2), 138.2 (C); GC-MS *m/z* 160 (1) [$M–H_2O^+$], 151 (9), 133 (54), 97 (86), 85 (40), 84 (38), 81 (7), 73 (48), 70 (36), 69 (100), 68 (99), 67 (25), 65 (13), 58 (17), 57 (45), 56 (30), 55 (45), 45 (17). Anal. Calcd for $C_7H_{12}O_4S$: C, 40.44; H, 5.66; S, 17.99. Found: C, 40.59; H, 5.81; S, 17.11.

Sultone **10c**. R_f 0.27 (pentane/EtOAc 1:2); colorless oil; IR 3517, 2935, 2861, 1344, 1247, 1159, 1142, 1031, 1010, 929, 902, 830, 750, 714, 657, 623 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.62–1.75 (m, 1 H), 1.93–2.11 (m, 3 H), 3.75 (dd, *J* = 0.8, 14.1 Hz, 1 H), 4.04 (d, *J* = 14.1 Hz, 1 H), 4.29–4.43 (m, 3 H), 5.52 (s, 1 H), 5.55 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.2 (CH_2), 30.3 (CH_2), 53.2 (CH_2), 71.7 (CH_2), 73.8 (CH), 123.7 (CH_2), 139.1 (C); GC-MS *m/z* 133 (83), 111 (41), 98 (14), 93 (6), 87 (36), 83 (14), 79 (10), 69 (100), 64 (13), 55 (24), 45 (14). HRMS *m/z* Calcd for $C_7H_{11}O_4S$ [$M–H^+$]: 191.0373. Found: 191.0392.

Red-Al reduction of hydroxy sultones 8 and 9 (general procedure)

To a stirred solution of the unsaturated hydroxy sultones **8a,b** (0.28 mmol) in toluene (7 mL) or **9a-c** (0.28 mmol) in CH_2Cl_2 (7 mL) cooled to −10 °C, Red-Al (70% in toluene, 0.11 mL, 0.33 mmol) was added all at once. Stirring was continued at 0 °C (**8a,b**) or −10 °C (**9a-c**) for the time listed in Scheme 2 and Table 3. The reaction mixture was treated with acetic acid/THF (1 mL, 1:1, v/v), stirred at room temperature for 15 min, and then was treated with saturated aqueous NH_4Cl (20 mL) at pH 4–5. Water (20 mL) was added, and the mixture was extracted with ethyl acetate (3x15 mL). The combined extracts were dried over $MgSO_4$, the solvents were removed in vacuo, and the crude product was purified by flash chromatography (EtOAc/pentane, 2:1) on silica gel to afford the saturated sultones **11a,b**, **13a-c**, and **14b,c**, respectively.

Red-Al reduction of epoxy sultones 6 and 7 (general procedure)

To a solution of the epoxy sultones **6a,b** or **7a-c** (0.4 mmol) in toluene (7 mL) cooled to −10 °C, Red-Al (70% in toluene, 0.16 mL, 0.48 mmol) was added portionwise with stirring. Stirring was continued at 0 °C for the time listed in Scheme 2 and Table 3. The mixture was then worked up and purified as above to afford the saturated sultones **11a,b**, **13a-c**, and **14b,c**, respectively.

Sultone **11a**: R_f 0.28 (EtOAc/pentane 2:1). IR 3516, 2930, 1418, 1336, 1153, 1039, 954, 777, 553 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (br s, 1 H), 2.05–2.27 (m, 4 H), 3.27 (ddd, J = 2.8, 8.3, 15.2 Hz, 1 H), 3.72 (ddd, J = 3.0, 9.7, 15.2 Hz, 1 H), 4.23–4.29 (m, 2 H), 4.49–4.54 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.6 (CH_2), 36.9 (CH_2), 46.2 (CH_2), 65.9 (CH_2), 66.6 (CH); GC-MS *m/z* 167 (21) [M+H$^+$], 149 (17), 138 (44), 121 (44), 110 (97), 83 (17), 73 (18), 57 (100), 46 (93), 28 (89). HRMS *m/z* Calcd for $C_5H_{11}O_4S$ [M+H$^+$]: 167.0373. Found: 167.0382.

Sultone **11b**: R_f = 0.35 (EtOAc/pentane 2:1); IR 3378, 2937, 1399, 1338, 1154, 924, 807 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (br s, 1 H), 1.76–1.84 (m, 1 H), 1.87–1.99 (m, 2 H), 2.06–2.18 (m, 2 H), 2.24–2.31 (m, 1 H), 3.21 (ddd, J = 1.9, 9.5, 15.5 Hz, 1 H), 3.50 (ddd, J = 1.8, 9.7, 15.5 Hz, 1 H), 4.06–4.11 (m, 1 H), 4.32–4.37 (m, 1 H), 4.41–4.46 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.4 (CH_2), 30.4 (CH_2), 32.2 (CH_2), 47.1 (CH_2), 69.1 (CH), 72.0 (CH_2); GC-MS *m/z* 181 (8) [M+H$^+$], 163 (33), 121 (62), 98 (8), 81 (45), 71 (92), 57 (85), 42 (100), 29 (43). HRMS *m/z* Calcd for $C_6H_{13}O_4S$ [M+H$^+$]: 181.0529. Found 181.0553. Anal. Calcd for $C_6H_{12}O_4S$: C, 39.99; H, 6.71; S, 17.79. Found: C, 40.14; H, 6.82; S, 17.64.

Sultone **13a**. R_f 0.20 (isohexane/EtOAc 1:1); IR 2969, 2935, 1716,1631, 1452, 1398, 1344, 1265, 1168, 1064, 956, 888, 831, 804, 763, 733, 706, 642 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.19 (d, J = 6.9 Hz, 3 H), 2.31–2.40 (m, 1 H), 2.85–2.92 (m, 2 H), 3.32 (dd, J = 4.2, 14.0 Hz, 1 H), 3.60 (dt, J = 4.3, 9.0 Hz, 1 H), 4.27 (dd, J = 9.1, 11.5 Hz, 1 H), 4.42 (dd, J = 4.3, 11.5 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.9 (CH_3), 35.9 (CH), 51.2 (CH_2), 68.4 (CH), 73.4 (CH_2); MS (ESI) *m/z* 184 [M+NH_4^+]; GC-MS *m/z*

136 (5), 125 (5), 107 (10), 72 (40), 57 (100). Anal. Calcd for $C_5H_{10}O_4S$: C, 36.14; H, 6.07; S, 19.29. Found: C, 36.26; H, 5.93; S 19.01.

Sultone **13b**. R_f 0.35 (CH_2Cl_2/EtOAc 1:4); ^{1}H NMR ($CDCl_3$) δ 1.23 (d, *J* = 7.2 Hz, 3 H), 2.06–2.12 (m, 1 H), 2.23–2.32 (m, 2 H), 3.18 (dd, *J* = 8.2, 15.2 Hz, 1 H), 3.66 (dd, *J* = 3.1, 15.2 Hz, 1 H), 3.85–3.88 (m, 1 H), 4.25 (ddd, *J* = 3.3, 6.8, 12.5 Hz, 1 H), 4.53 (ddd, *J* = 2.6, 8.6, 12.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.8 (CH_3), 34.8 (CH_3), 35.6 (CH), 53.3 (CH_2), 65.9 (CH_2), 72.5 (CH); MS (ESI) *m/z* 198 [M+NH_4^+]; GC-MS *m/z* 153 (4), 135 (11), 121 (78), 110 (5), 99 (4), 93 (4), 83 (74), 75 (84), 69 (15), 64 (4), 57 (100), 46 (19).

Sultone **13c**. R_f 0.36 (CH_2Cl_2/EtOAc 1:4); mp 49–51 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (d, *J* = 7.0 Hz, 3 H), 1.86–1.92 (m, 1 H), 1.92–1.97 (m, 1 H), 1.99–2.02 (m, 1 H), 2.03–2.10 (m, 1 H), 2.23–2.28 (m, 1 H), 3.18 (dd, *J* = 7.3, 15.6 Hz, 1 H), 3.24 (dd, *J* = 2.5, 15.6 Hz, 1 H), 3.66–3.69 (m, 1 H), 4.32–4.37 (m, 1 H), 4.44–4.50 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.1 (CH_3), 22.9 (CH_2), 30.7 (CH_2), 35.6 (CH), 54.3 (CH_2), 72.0 (CH_2), 74.6 (CH); MS (ESI) *m/z* 212 [M+NH_4^+]; GC-MS *m/z* 152 (1), 135 (20), 97 (4), 87 (5), 83 (5), 79 (1), 71 (100), 67 (2), 57 (21), 53 (3), 45 (4).

Sultone **14b**. R_f 0.47 (CH_2Cl_2/EtOAc 1:4); IR 3532, 2971, 2922, 1333, 1155, 1089, 992, 935, 902, 820, 716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (d, *J* = 7.2 Hz, 3 H), 1.90–1.99 (m, 1 H), 2.19–2.25 (m, 1 H), 2.27–2.36 (m, 1 H), 3.00 (ddd, *J* = 0.6, 2.1, 15.0 Hz, 1 H), 3.72 (dd, 1 H, *J* = 11.0, 15.0 Hz), 3.98 (br s, 1 H), 4.18–4.25 (m, 1 H), 4.47–4.55 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.5 (CH_3), 33.8 (CH), 36.0 (CH_2), 51.5 (CH_2), 65.4 (CH_2), 70.6 (CH); MS (ESI) *m/z* 198 [M+NH_4^+]; GC-MS *m/z* 151 (3), 135 (14), 124 (19), 121 (79), 83 (63), 75 (81), 73 (15), 71 (20), 69 (16), 65 (10), 57 (100), 56 (15), 55 (13), 45 (37).

Sultone **14c**. R_f 0.44 (CH_2Cl_2/EtOAc 1:4); mp 62–70 °C; IR 3521, 2999, 2967, 2942, 1327, 1225, 1150, 1123, 988, 954, 917, 847, 802, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (d, *J* = 7.3 Hz, 3 H), 1.55 (s, 1 H), 1.70–1.76 (m, 1 H), 1.87–1.94 (m, 1 H), 1.97–2.04 (m, 1 H), 2.13–2.17 (m, 1 H), 2.43–2.47 (m, 1 H), 2.90 (dd, *J* = 1.5, 15.6 Hz, 1 H), 3.64 (dd, *J* = 8.7, 15.6 Hz, 1 H), 3.92–3.95 (m, 1 H), 4.33 (ddd, *J* = 4.8, 9.4, 14.2 Hz, 1 H), 4.41–4.45 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.1 (CH_3), 21.6 (CH_2), 31.1 (CH_2), 34.0 (CH), 51.8 (CH_2), 71.7 (CH_2), 71.8 (CH); MS (ESI) *m/z* 212 [M+NH_4^+]; GC-MS *m/z* 152 (1), 135 (21), 71 (100), 69 (6), 65 (2), 57 (19), 45 (4), 43 (35), 42 (50), 41 (28).

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